



TITLE:

# Cyclopropanes. (XI). Solvent Effect in Partial Asymmetric Synthesis

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## ABSTRACTS

thetic organic reactions which involve metal alkoxides and carbonyl compounds. It was assumed that the coordination of aldehyde to the metal alkoxide was essential in propagation reaction which determined the stereospecificity of the polymer produced.

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### Cyclopropanes. (XI). Solvent Effect in Partial Asymmetric Synthesis

YUZO INOUE, Shuji INAMASU, Minoru OHNO, H. M. WALBORSKY  
and Toshio SUGITA

*Journal of the American Chemical Society*, **83**, 2962 (1961)

Partial asymmetric syntheses were achieved by the base catalyzed Michael type addition of (–)-menthyl chloracetate to ethyl acrylate. It is not surprising since partial asymmetric syntheses have been reported by the present authors in mechanistically similar condensations of the  $SN_2$ -process: *e.g.* the non-catalytic addition of diazo-compounds to  $\alpha,\beta$ -unsaturated menthyl esters and the Darzens reactions of (–)-menthyl chloracetate with carbonyl compounds leading to glycidic acids. However, changing the solvent medium from poor solvating and low dielectric solvents such as toluene, benzene, diethyl ether, *n*-octane, cyclohexane and decalin to strongly solvating and high dielectric solvents such as N,N-dimethylformamide, hexamethylphosphortriamide, dimethylsulfoxide and nitrobenzene, resulted in a complete reversal of sign in the resulting optically active *trans*-cyclopropane-1,2-dicarboxylic acid. The Michael type condensation in non-polar solvents gave laevorotatory acid in 1.8~3.1% optical yields, whilst in polar solvents the enantiomeric dextrorotatory acid was obtained in markedly better optical yields, 10~11%.

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### New $\gamma$ -Glutamyl Peptides in Garlic

TOMOJI SUZUKI, Michiyasu SUGI and Toshio KAKIMOTO

*Chemical and Pharmaceutical Bulletin*, **9**, 77 (1961)

During hydroponic cultivation of garlic (*Allium sativum*) by using  $^{35}SO_4^{2-}$  for tracer studies, considerable amount of  $^{35}S$ -labeled S-allylcysteine sulfoxide (alliin), S-methylcysteine sulfoxide and 3-methyl-1,4-thiazane-5-carboxylic acid 1-oxide (cycloalliin) were observed.

Besides these  $^{35}S$ -containing amino acids, six new  $\gamma$ -glutamyl peptides were separated. Of these peptides, four were identified as  $\gamma$ -glutamyl-phenylalanine,  $\gamma$ -glutamyl-S-methylcysteine,  $\gamma$ -glutamyl-S-methylcysteine sulfoxide and  $\gamma$ -glutamyl-S- $\beta$ -carboxy- $\beta$ -methylethylcysteinyglycine (S-(2-carboxypropyl) glutathione).

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